

# Modeling the Modification Depth of Carbon Dioxide Laser-Treated Dental Enamel

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**Background and Objectives:** Many studies of laser-induced thermal decomposition of dental enamel have demonstrated a reduction in the rate of acid dissolution, size of artificial caries-like lesions, and acid reactivity. Additionally, studies have correlated the loss of carbonate from dental enamel with a reduction in acid dissolution. Dental mineral consists of hydroxyapatite with many substitutions, the major one being carbonate (~ 3–5% by weight), which markedly affects acid reactivity. The principle objective of the present work was to determine the precise depth of modification, i.e., thermally induced decomposition of dental enamel (carbonate loss), at the predicted optimum laser irradiation parameters.

**Study Design/Materials and Methods:** Bovine enamel blocks were irradiated at  $\lambda = 9.6 \mu\text{m}$  with 2- $\mu\text{sec}$  and 100- $\mu\text{sec}$  pulses and at  $\lambda = 10.6 \mu\text{m}$  with 2- $\mu\text{sec}$  pulses. Carbonate loss was calculated from infrared spectra as a function of depth and compared to numerical simulations of the maximum temperature rise.

**Results:** Carbonate loss was initiated at temperatures greater than 400°C, but was complete only after repeated irradiation of the surface above the melting threshold. Carbonate loss of dental enamel irradiated at 9.6  $\mu\text{m}$  with a 100- $\mu\text{sec}$  pulse and at 10.6  $\mu\text{m}$  with a 2- $\mu\text{sec}$  pulse was greater than that of enamel irradiated at 9.6  $\mu\text{m}$  with a 2- $\mu\text{sec}$  pulse. The depth of carbonate loss in dental enamel irradiated with a 2- $\mu\text{sec}$  pulse was greater for  $\lambda = 10.6 \mu\text{m}$  than for  $\lambda = 9.6 \mu\text{m}$ .

**Conclusion:** The depth of modification is consistent with the presented model that incorporates the absorption depth and thermal relaxation time/pulse duration. However, repeated irradiation is required for complete removal of carbonate, depending on absorption depth and pulse duration. *Lasers Surg. Med.* 25:335–347, 1999. © 1999 Wiley-Liss, Inc.

**Key words:** infrared; spectroscopy; laser; heating; carbonate; depth profile; dental enamel

## INTRODUCTION

Despite the great advances in oral health and hygiene, dental caries (dental decay) continues to affect a large portion of the population in the United States [1]. Dental caries originates when acids produced through carbohydrate metabolism by dental plaque bacteria diffuse into the tooth and begin dissolving the enamel mineral. Dental mineral is a highly substituted form of hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , commonly re-

ferred to as carbonated apatite and represented by the simplified formula,  $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-y}(\text{CO}_3)_y(\text{OH})_{2-u}(\text{F})_u$  [2]. Although many different elements and functional groups have been found substituting

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for the hydroxyapatite components of the calcium, phosphate, and hydroxyl groups, three common substitutions are expressed in the formula. The most prevalent substitution is that of carbonate in place of the phosphate group. In normal enamel, the carbonate content is approximately 3–5% by weight [3]. At a given pH, the solubility of hydroxyapatite is approximately an order of magnitude below that of carbonated apatite. If the substitution of fluoride for the hydroxyl group is complete, fluorapatite results,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$ , which is another order of magnitude less soluble than hydroxyapatite.

Several studies over the past 30 years have demonstrated the potential of laser treatment of dental enamel to inhibit acid dissolution or artificial caries-like lesions [4–15]. Other studies have shown a decrease in acid reactivity due to laser treatment of dental enamel or hydroxyapatite [14,16]. Conventional heating experiments showed that approximately 30% of the carbonate was eliminated from dental enamel at temperatures between 400–600°C [17], and further carbonate loss occurred at higher temperatures. Recent studies in our laboratory indicated a direct correlation between carbonate loss in laser-treated dental enamel and a corresponding reduction in the rate of acid dissolution. The loss of carbonate results in a mineral phase which more closely resembles hydroxyapatite and is therefore less soluble than normal enamel at any given pH [18]. Previous studies showed a similar correlation in artificial apatites with varying carbonate content [2,19].

A major clinical concern with laser irradiation of teeth is the potential for overheating the tooth pulp that could lead to pulpal necrosis [20]. Carbon dioxide lasers are highly absorbed by enamel; therefore, the initial temperature rise occurs in a thin layer near the surface. Previous studies have shown that  $\text{CO}_2$  laser irradiation will not cause thermal injury to the pulp if the total energy delivered in a few seconds is less than 4–8 J [21–23]. In the current study, multiple short pulses (2- or 100- $\mu\text{sec}$  duration) with a total energy of less than 1 J delivered to any given spot were used to minimize heat deposition and prevent pulpal damage.

For temperature changes at the surface of the tooth, the duration of time over which the energy is delivered is equal in importance to the amount of energy delivered. To illustrate this, consider two extreme cases for a thermally isolated enamel block. In the first example, assume all of the energy is delivered as an instantaneous

pulse. The initial temperature rise at any depth will be dependent only upon the absorption properties of the enamel at the irradiating wavelength. As an example, consider a hypothetical case where all of the energy is absorbed uniformly within a layer 10  $\mu\text{m}$  (0.001 cm) deep. This thickness is approximately equal to the enamel absorption depth of light with a wavelength of 10.6  $\mu\text{m}$ . Assume 1 J is delivered to one surface of a solid enamel block 1  $\times$  1  $\times$  1 cm. The heat capacity of enamel is  $c = 0.75 \text{ J/(g } ^\circ\text{C)}$  and the density of enamel is  $\rho = 2.9 \text{ g/cm}^3$  [24]. The temperature rise of the heated volume is

$$\Delta T = \frac{E}{\rho c A z}$$

where  $E$  is the energy delivered,  $A$  is the surface area, and  $z$  is the depth of heating. The instantaneous temperature rise will be 460°C in the 10- $\mu\text{m}$  layer near the surface. Subsequently, the thermal energy diffuses to the remainder of the enamel block and eventually heats the entire block to a mere 0.460°C.

In the second case, consider the same amount of energy delivered to the isolated block continuously over an extended period of time far longer than needed for heat equilibration in the enamel block. As the first 10  $\mu\text{m}$  is slowly heated, the energy flows to the rest of the block. After 1 J of energy is delivered, the entire block will have a temperature rise of 0.460°C. To raise the surface temperature 460°C, 1,000 J of energy is needed, which heats the entire block and would certainly cause necrosis of the pulp if it were present.

In the first case, there would be a therapeutic effect in a thin layer near the surface, but the region that would contain the pulp has a minimal temperature rise. In the second case, there will be no effect other than the slight temperature rise throughout the entire block. The aim of our study was to maximize the benefit of laser treatment by heating a layer of the appropriate thickness to a sufficiently high temperature while causing minimal thermal insult to the deeper layers of the tooth. These requirements are more stringent than merely avoiding thermal injury of the pulp.

The preceding two examples lead to the concept of thermal relaxation time. The thermal relaxation time of a material is a characteristic time in which heat is conducted from a small volume. The thermal relaxation time can be defined in many ways, and one definition traces its origin to the analytical solution of the one-dimensional

equation of heat conduction into a homogeneous, semi-infinite medium under the boundary condition of constant surface temperature, surface heat flux, or surface convection. If the one-dimensional, transient heat conduction equation,

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c} \frac{\partial^2 T}{\partial x^2} \quad (1)$$

is solved analytically with a constant surface temperature as the boundary condition, the temperature distribution is given by

$$\frac{T(x,t) - T_s}{T_i - T_s} = \text{erf} \left[ \frac{x}{\sqrt{4Kt}} \right] \quad (2)$$

where  $T(x,t)$  is the temperature at a depth ( $x$ ) from the surface at time  $t$ .  $K$  is the thermal diffusivity.  $T_s$  is the surface temperature at time  $t > 0$ .  $T_i$  is the initial temperature of the semi-infinite solid. Erf is the Gaussian error function.

By setting

$$\frac{x}{\sqrt{4Kt}} = 1$$

and solving for  $t$ , the characteristic thermal relaxation time can be defined by

$$t = \frac{x^2}{4K}$$

In this case, the thermal relaxation time is the time it takes for the temperature at a given depth ( $x$ ) to reach a temperature which is approximately 84% of the difference between the surface temperature and the initial temperature, since  $\text{erf}(1) = 0.84270$ .

The same equation,

$$t = \frac{x^2}{4K}$$

can be used to define the thermal relaxation time during pulsed laser heating. The length ( $x$ ) is defined by the absorption depth of the material for a given wavelength  $\lambda$ ,

$$x(\lambda) = \frac{1}{\mu_a(\lambda)}$$

where  $\mu_a(\lambda)$  = the absorption coefficient at  $\lambda$ . At this depth, the intensity of irradiating light has been reduced to  $1/e$  times that of the intensity at the surface. The thermal relaxation time represents an estimate of the time required for thermal diffusion to reduce the temperature in a layer of thickness ( $x$ ) by approximately one half. If the pulse duration of the laser is on the order of or less than the thermal relaxation time, the energy will remain in the volume where it was absorbed. Since the energy is not leaving this region, large temperature increases near the surface can be realized with low energy input, similar to the case of instantaneous heating. If the pulse duration is much longer than the thermal relaxation time, the thermal energy will flow towards the center of the tooth and heat a larger volume to a lower temperature that may or may not be large enough for a therapeutic effect.

The present study was conducted to correlate the temperature rise in dental enamel due to pulsed laser irradiation with chemical changes in the enamel as a function of depth. This study will help determine how the depth of modified tissue affects acid dissolution rate and in vitro caries-like lesion progression. The overall objective of the studies in our laboratory is to determine the appropriate laser parameters to irradiate enamel in vivo that may cause a reduction in caries and caries progression.

## MATERIALS AND METHODS

### Numerical Modeling

Numerical simulations of heat conduction in dental enamel, employing recent data of absorption coefficients and thermal properties of dental enamel, were used to estimate the temperature rise in dental enamel due to pulsed laser irradiation. These simulations were initially employed to estimate unknown absorption coefficients of dental enamel by comparing the experimentally measured thermal emission of laser-irradiated dental enamel with model calculations [25]. The model was confirmed by comparing its thermal emission predictions with the experimentally measured thermal emission of dental enamel irradiated at wavelengths with known absorption coefficients. Using thermal emission and direct transmission measurements, the absorption coefficients of dental enamel were determined to be approximately  $8,000 \text{ cm}^{-1}$  at  $9.6 \text{ } \mu\text{m}$  and  $825 \text{ cm}^{-1}$  at  $10.6 \text{ } \mu\text{m}$  [25].

These numerical simulations consider the temporal laser pulse shape and fluence as well as

TABLE 1. Relevant Properties of Dental Enamel

Wavelength	9.6 $\mu\text{m}$	10.6 $\mu\text{m}$
Bovine enamel reflectance (air/tissue interface) [23]	0.487	0.138
Absorption coefficient [20]	8,000 $\text{cm}^{-1}$	825 $\text{cm}^{-1}$
Absorption depth (1/e)	1.3 $\mu\text{m}$	12 $\mu\text{m}$
Thermal relaxation time, one-dimensional axial heat conduction (spot size $\gg$ absorption depth)	1 $\mu\text{sec}$	90 $\mu\text{sec}$

the thermal and optical properties of dental enamel, including the absorption coefficient at the incident wavelength. Since the beam diameter (0.5–2.0 mm) is much larger than the heated depth (0.1 mm) during the time modeled, the one-dimensional heat conduction equation served as the basis for the computer model,

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c} \cdot \frac{\partial^2 T}{\partial z^2} + \frac{F(t,z)}{\rho c} \quad (3)$$

where  $T$  is the temperature rise,  $t$  is the time,  $z$  is the depth,  $k$  is the thermal conductivity,  $\rho$  is the density of enamel,  $c$  is the specific heat capacity, and  $F(t,z)$  is the temporally and spatially dependent power delivered to the enamel by the laser pulse. The thermal constants for dental enamel are  $\rho = 2.9 \text{ g/cm}^3$ ,  $c = 0.75 \text{ J/(g } ^\circ\text{C)}$ , and  $k = 9.2 \times 10^{-3} \text{ W/(cm } ^\circ\text{C)}$  [24]. Equation (3) was solved numerically on a personal computer using the Crank-Nicholson implicit finite difference technique [26].

In the portion of the infrared spectrum of relevance (9–11  $\mu\text{m}$ ), dental enamel is highly absorbing and scattering may be ignored. The spatial portion of the dependence of energy deposition,  $F(t,z)$ , follows the Beer-Lambert law, thus

$$F(t,z) = (1 - R) \cdot F(t) \cdot \mu_\alpha \cdot \exp[-\mu_\alpha \cdot z] \quad (4)$$

where  $R$  is the measured reflectivity at the incident wavelength [27],  $\mu_\alpha$  is the absorption coefficient of enamel at the irradiation wavelength (Table 1),  $z$  is the depth from the surface into the enamel, and  $F(t)$  is the temporal profile of the laser pulse power density.  $F(t)$  was implemented in the computer model by digitizing the actual laser pulse measured with a custom-built pyroelectric detector with a response time less than 500 psec.

The modeled thickness was 100  $\mu\text{m}$ , with 0.05- $\mu\text{m}$  spacing. The length of time modeled was

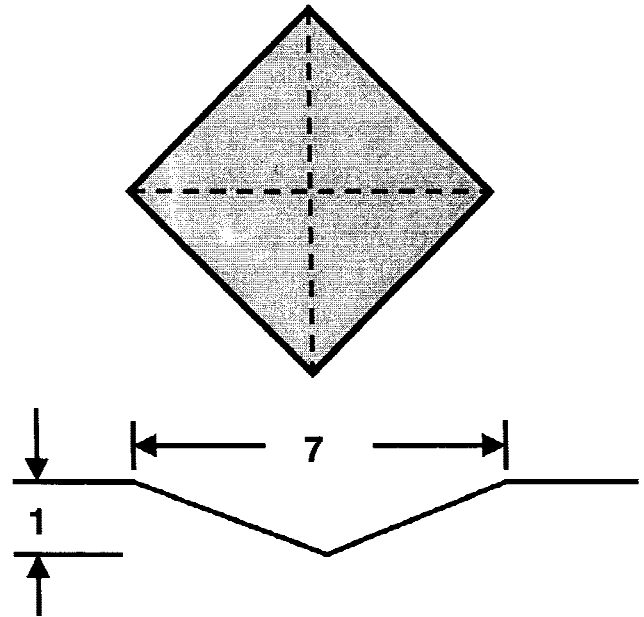


Fig. 1. The depth of the indent is one seventh the length of the diagonal of the diamond-shaped indent, which can be measured under a microscope. After polishing, the indent is remeasured to determine the thickness of the material removed.

100  $\mu\text{sec}$  at 0.05- $\mu\text{sec}$  intervals for the 2- $\mu\text{sec}$  pulse at 9.6  $\mu\text{m}$ , and 1 msec at 0.175- $\mu\text{sec}$  intervals for the 2- $\mu\text{sec}$  pulse at 10.6  $\mu\text{m}$  and the 100- $\mu\text{sec}$  pulse at 9.6  $\mu\text{m}$ . No heat loss was assumed at the front and back surface. A worst-case analysis indicated that convection losses could be ignored and that radiation losses during the time of the simulation were less than 1% of the deposited energy. The temperature rise at the back surface was  $<1^\circ\text{C}$ , so heat accumulation did not affect the temperature near the front of the enamel block.

### Experimental Overview

The measurement of carbonate loss as a function of depth consisted of several steps: 1) Dental enamel blocks were irradiated with a  $\text{CO}_2$  laser. 2) The enamel was indented with a Vickers microhardness indenter. 3) The lengths of the indents were measured. 4) Infrared reflectance spectroscopy was performed on the laser treated enamel. 5) The enamel was polished to remove approximately 1  $\mu\text{m}$  of material. 6) The indents were remeasured to determine the actual depth of material lost. Steps 4–6, spectroscopy, polishing, and indent measurement were repeated until there was no further change in carbonate content. Each step is outlined in greater detail below.

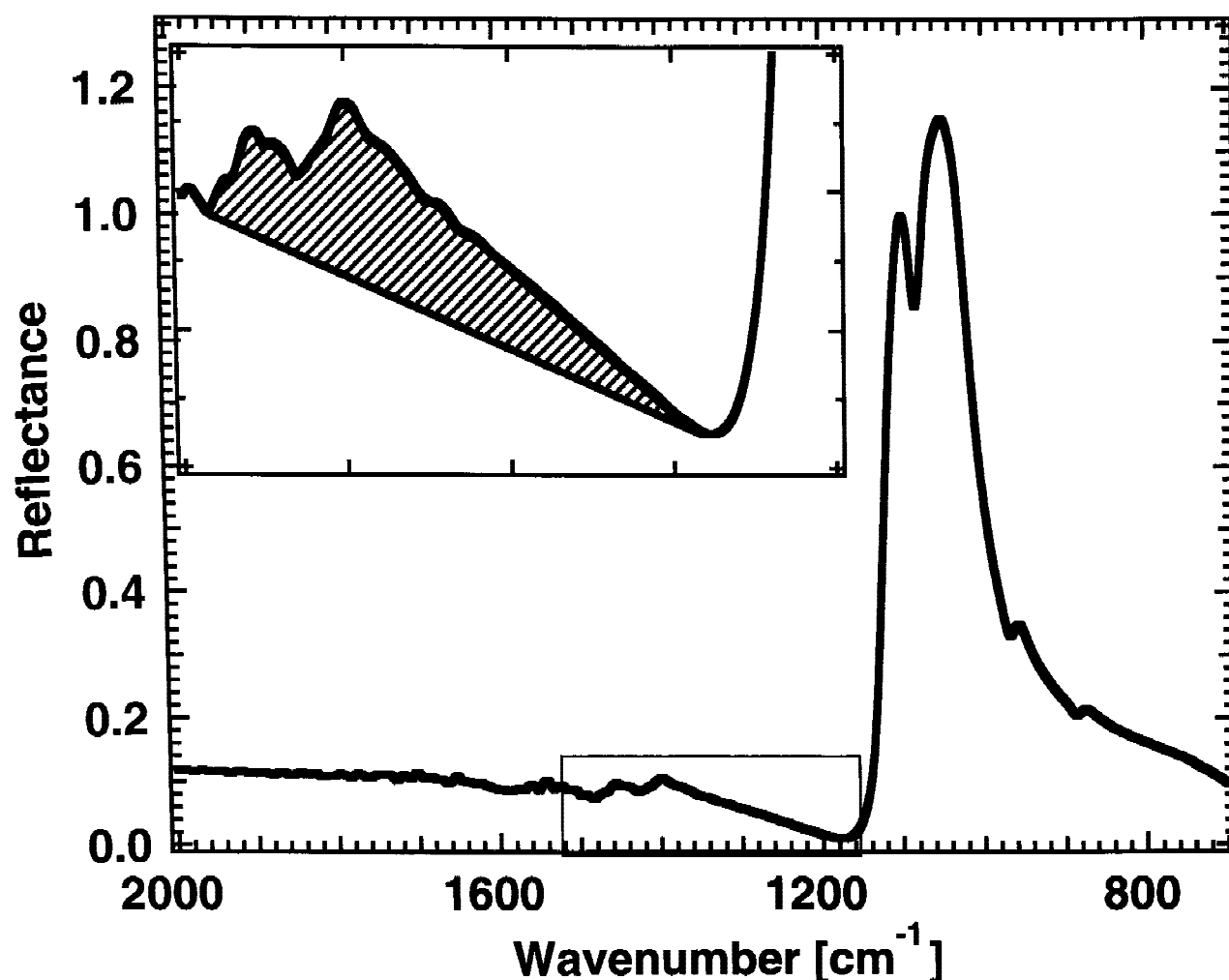


Fig. 2. The dental enamel spectrum has a strong band which corresponds to the phosphate groups near  $1,000\text{ cm}^{-1}$ . This study concentrated on the smaller carbonate band near  $1,400\text{ cm}^{-1}$ , enlarged in the inset. The area between the carbonate peaks and the baseline was calculated to assess the amount of carbonate present in the irradiated dental enamel.

#### Irradiation of Dental Enamel

Sound bovine enamel blocks ( $5 \times 5 \times 2\text{ mm}$ ) were serially polished with 6-, 3-, and  $1\text{-}\mu\text{m}$  diamond suspension solutions. Bovine enamel was used as a model of human enamel for several reasons. Bovine teeth are much bigger than human teeth; therefore large, flat surfaces could be prepared. The reflectance of bovine enamel in the infrared has been shown to be similar to the reflectance of human enamel [27,28]. Bovine enamel has also been used in other laboratories for the study of caries [29,30]. The progression rate of artificial caries is greater in bovine enamel than in human enamel, but the mechanism is similar [31]. The enamel blocks were irradiated with either a  $\text{CO}_2$  laser (Pulsed Systems, Los Alamos, NM) with a  $100\text{-}\mu\text{sec}$  pulse duration at  $1\text{ Hz}$ ,

wavelength of  $9.6\text{ }\mu\text{m}$ , and fluence of  $4\text{ J/cm}^2$ , or a transversely excited, atmospheric (TEA)- $\text{CO}_2$  (Argus Photonics Group, Jupiter, FL) laser with a  $2\text{-}\mu\text{sec}$  pulse duration at  $0.5\text{ Hz}$ , wavelength of either  $9.6$  or  $10.6\text{ }\mu\text{m}$ , and fluence of  $2\text{ J/cm}^2$  or  $4\text{ J/cm}^2$ , respectively. The spatial profile of the beams was Gaussian. The laser energy was measured with a laser calorimeter (Model ED-200, Gentech, Ste-Foy, Quebec). The laser spot size (full width at  $e^{-2}$ ) was measured by scanning the beam with a razor blade. Since a Gaussian beam has a spatially variable local fluence, the nominal fluence listed above was the local fluence at the center of the beam, which is twice the average fluence of the beam based on the pulse energy divided by the area of the beam.

Two different methods were used to irradiate



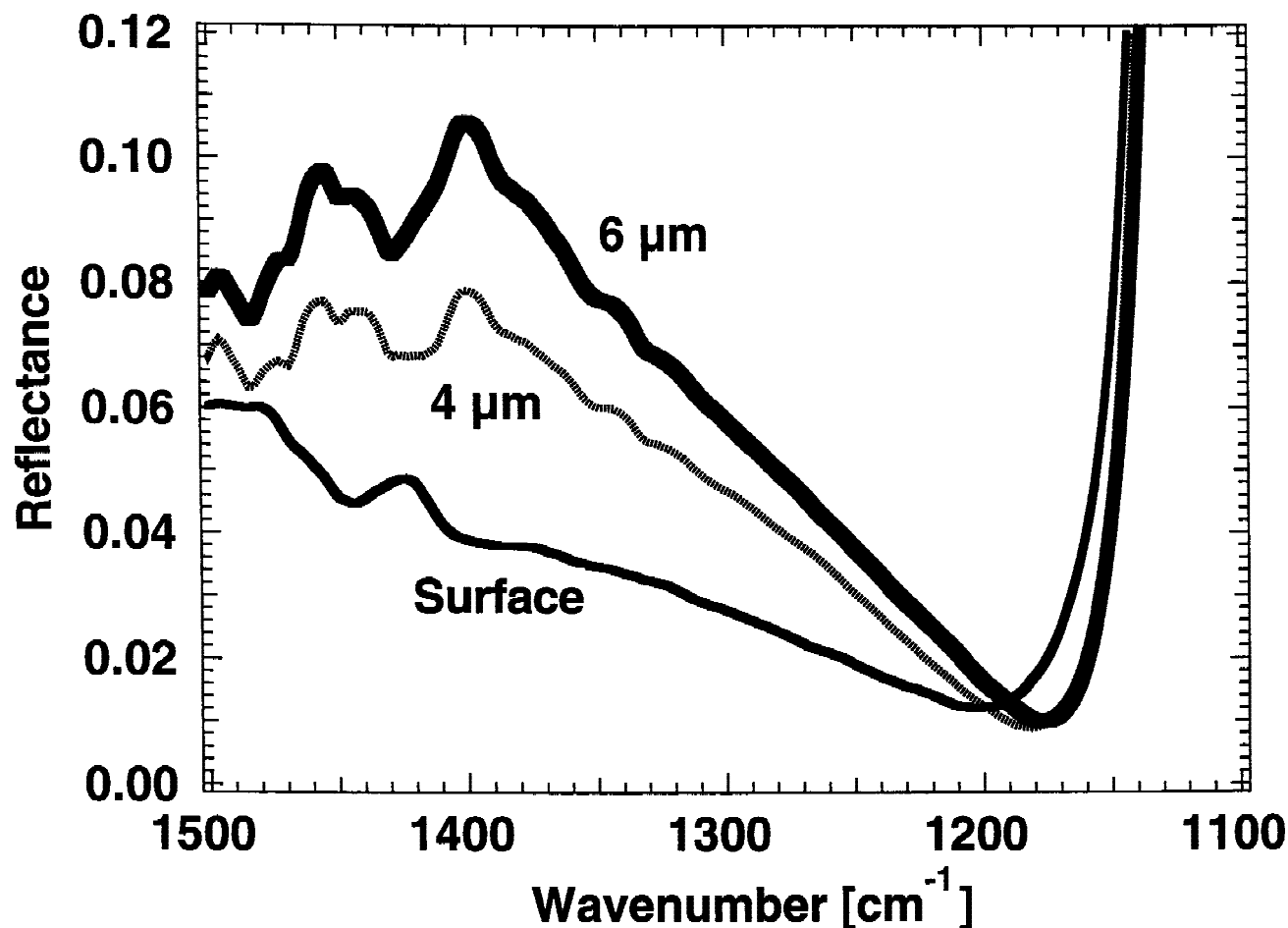


Fig. 3. After irradiation, the carbonate peaks have disappeared at the surface (thin solid line). The peaks return to full intensity after removing approximately 6  $\mu\text{m}$  of material (thick line). At an intermediate depth, 4  $\mu\text{m}$  (thin dashed line), the carbonate peaks have intermediate intensity.

the enamel in order to homogenize the fluence across the surface. In the first method, a 0.5-mm beam was scanned in two dimensions across the surface of the enamel block. The spacing between spots was small, so that the minimum fluence at any point was 0.85 times the nominal fluence based on a Gaussian spatial beam profile. In the second method, dental enamel was irradiated with a single large spot ( $\sim 2$  mm). Since the aperture of the infrared (IR) microscope (see Infrared Spectroscopy, below) was  $150 \times 150 \mu\text{m}$ , the minimum fluence at the edge of the aperture was 0.9 times the nominal fluence.

#### Indentation and Depth Measurement

After irradiation, the enamel was indented near the laser-treated areas with a Vickers microhardness indenter (Fig. 1). A Vickers indenter is a diamond pyramid with a square base. The depth

of penetration equals one seventh of the diagonal of indentation. The lengths of the diagonals of the diamond-shaped indent were measured using an integrated computer imaging and optical microscope system. The enamel was subsequently polished using a 1- $\mu\text{m}$  diamond suspension to remove approximately 1  $\mu\text{m}$  of enamel from the surface. The lengths of the indents were remeasured after polishing. Measuring the reduction in length of the diagonal allowed calculation of the thickness of material removed.

#### Infrared Spectroscopy

An infrared microscope (XAD plus, Laser Precision Analytical, Irvine, CA) with a  $150 \times 150 \mu\text{m}$  aperture attached to a Fourier transform infrared spectrometer (Model RFX-30, Laser Precision Analytical, Irvine, CA) was used to obtain infrared spectra of untreated and laser-treated

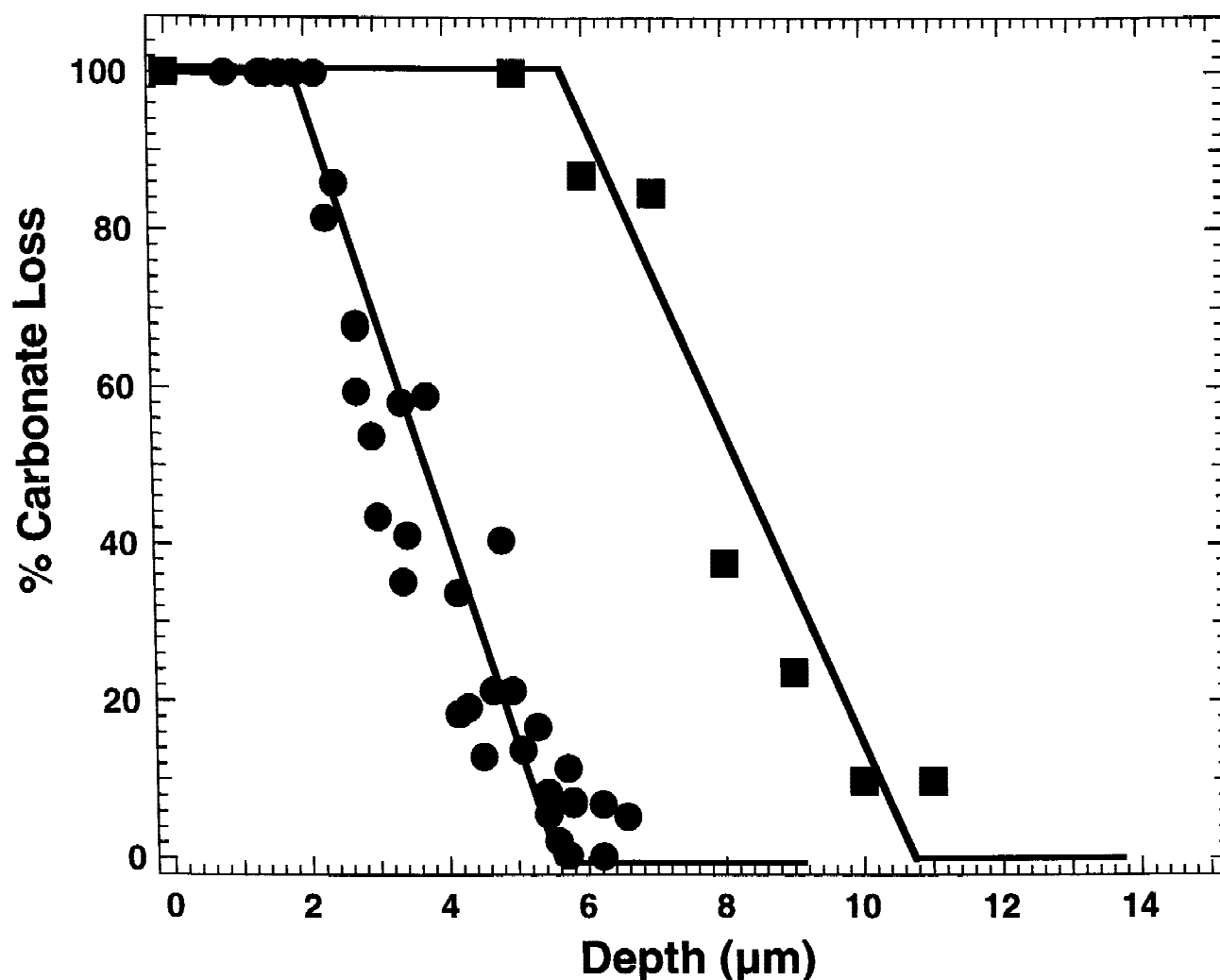


Fig. 4. Percent carbonate loss, as a function of depth for enamel irradiated at 9.6  $\mu\text{m}$ . The surface was scanned with 100- $\mu\text{sec}$  pulses at 4  $\text{J}/\text{cm}^2$  (squares) or 2- $\mu\text{sec}$  pulses at 1  $\text{J}/\text{cm}^2$ . The lines show trends in the data and are not mathematical fits.

dental enamel near the microhardness indents (Fig. 2). Spectra were obtained after irradiation and between iterations of polishing. To estimate the carbonate content of the dental enamel, the area between the infrared spectra of the carbonate region (1,200–1,500  $\text{cm}^{-1}$ ) and the baseline (Fig. 2) were calculated at each depth. The strength of the reflectance in this region of the infrared spectrum of dental enamel is due to the doubly degenerate  $\nu_3$  stretching mode of the carbonate ion [32]. The carbonate loss was calculated,

$$\% \text{ carbonate loss} = 100 (1 - A_t/A_u) \quad (5)$$

where  $A_t$  is the area of the carbonate band for a given set of treatment conditions and a given

depth, and  $A_u$  is the area of the carbonate band for untreated enamel. When no carbonate peaks were present, the integral was not calculated because it became meaningless and simply reflected remaining noise, often indicating that more than 100% of the carbonate was removed.

## RESULTS

An example of the dependence of the strength of the carbonate band upon depth is illustrated in Figure 3. At the surface, the carbonate has been completely removed, and thus the two predominant carbonate peaks present at greater depths are absent. The area under the carbonate band increased as a function of depth until it equaled the area under the carbonate band of enamel before laser treatment.

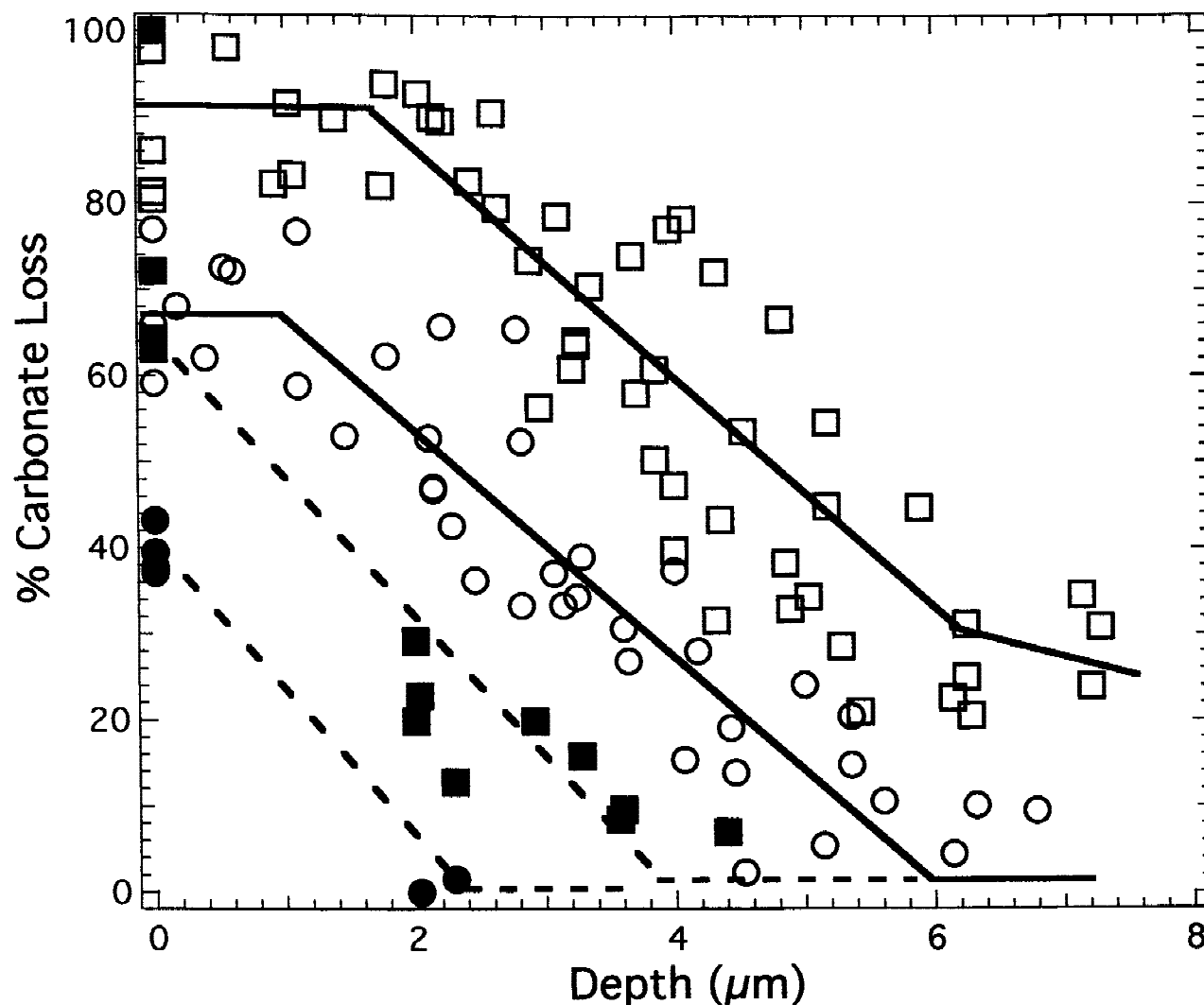


Fig. 5. Percent carbonate loss, as a function of depth for enamel irradiated with 2- $\mu$ sec pulses. One large spot was irradiated at 9.6  $\mu$ m, 2 J/cm<sup>2</sup> with one pulse (solid circles) and five pulses (open circles) and at 10.6  $\mu$ m, 4 J/cm<sup>2</sup> with one pulse (solid squares) and five pulses (open squares). The lines show trends in the data and are not mathematical fits.

After irradiating dental enamel at 9.6  $\mu$ m with either 2- $\mu$ sec or 100- $\mu$ sec pulses, the percent carbonate loss was calculated as a function of depth (Fig. 4). The lines drawn in Figure 4 are meant to show trends in the data and should not be interpreted as a mathematical fit. Each spot was treated with five pulses, and the laser was scanned across the surface in two dimensions. At the surface, complete carbonate loss was observed in dental enamel irradiated by either pulse duration. The carbonate loss remained complete near the surface and then decreased as a function of depth until it was essentially zero at 6  $\mu$ m for the 2- $\mu$ sec pulse and zero at 11  $\mu$ m for the 100- $\mu$ sec pulse.

After irradiating a single large spot ( $\sim$ 2 mm FW at  $e^{-2}$ ) on enamel blocks with a 2- $\mu$ sec laser pulse at 9.6  $\mu$ m or 10.6  $\mu$ m, the percent carbonate loss was measured as a function of depth (Fig. 5). At the surface, 100% carbonate loss was only achieved with the 9.6- $\mu$ m wavelength and 2- $\mu$ sec pulses after 10–20 pulses irradiated the same spot. The surface of enamel irradiated at 9.6  $\mu$ m lost an average of 76% and 40% carbonate for five pulses and one pulse, respectively. The carbonate loss of enamel irradiated with five pulses steadily decreased as a function of depth until there was essentially no carbonate loss at 6  $\mu$ m. Irradiating with a single pulse, the carbonate loss fell to zero within 2  $\mu$ m of the surface. The surface of enamel



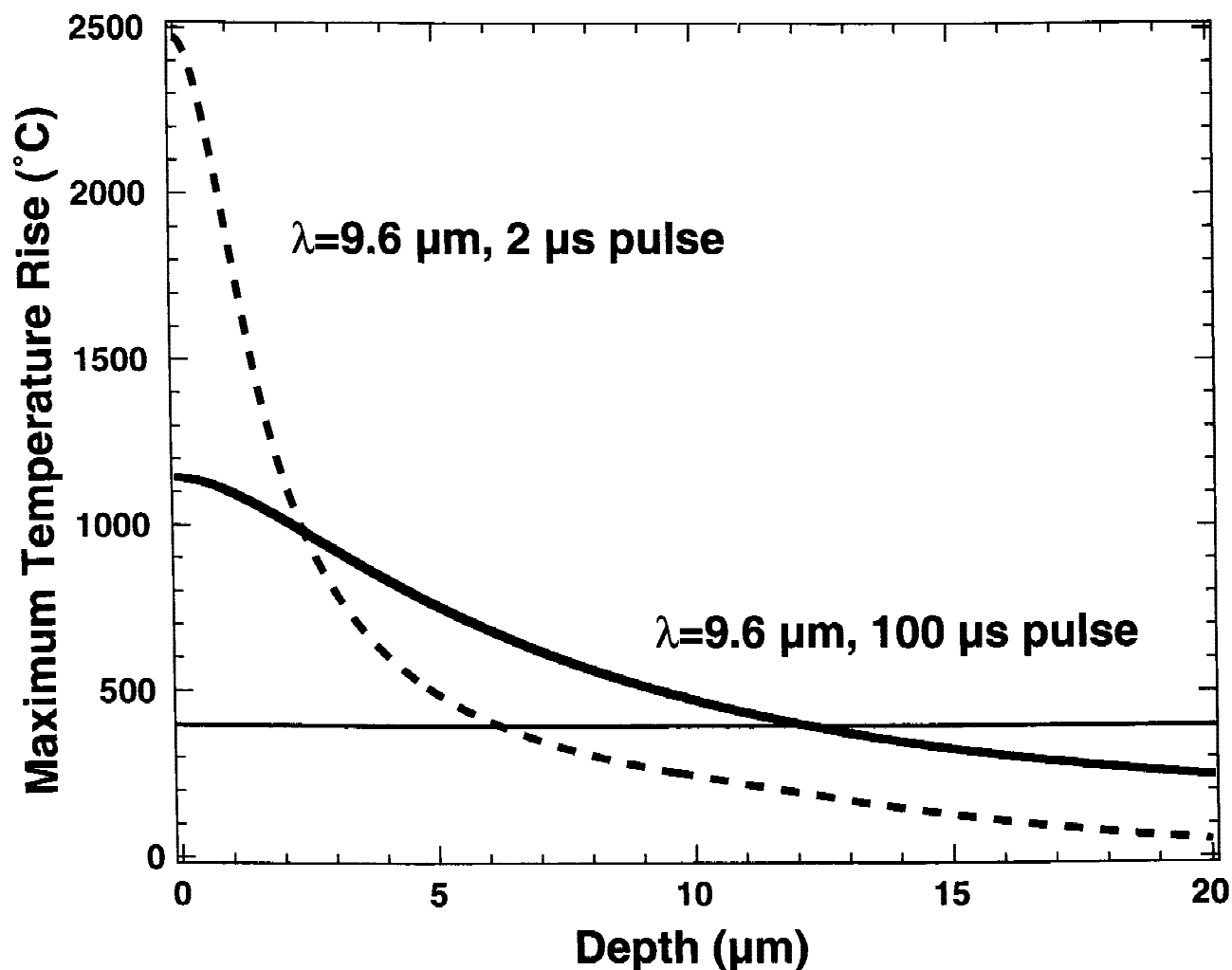


Fig. 6. The maximum temperature rise vs. depth was calculated for enamel irradiated at 9.6  $\mu\text{m}$  with a 100- $\mu\text{sec}$  pulse at 4  $\text{J}/\text{cm}^2$  (curved solid line) and a 2- $\mu\text{sec}$  pulse at 2  $\text{J}/\text{cm}^2$  (dashed line). At 400°C, a horizontal line is drawn indicating the temperature at which carbonate loss is initiated. The depth of initiation predicted for each condition (6  $\mu\text{m}$  for 2- $\mu\text{sec}$  pulse and 11  $\mu\text{m}$  for 100- $\mu\text{sec}$  pulse) corresponds to the depth determined experimentally (Fig. 5).

irradiated at 10.6  $\mu\text{m}$  lost 100% and 66% of the carbonate for five pulses and one pulse, respectively. The carbonate loss decreased from the surface into the bulk until there was no carbonate loss at 5  $\mu\text{m}$  for one pulse. At 8- $\mu\text{m}$  depth, the percent carbonate loss remained almost 30% for the enamel irradiated with five pulses.

## DISCUSSION

Brittle materials such as dental enamel cannot be cut into ultrathin sections to obtain depth-resolved chemical and physical information with 1- $\mu\text{m}$  accuracy. The method presented in this paper is a novel method of acquiring such informa-

tion about these materials. This technique was used to obtain chemical information from infrared spectroscopy, but it may be generalized to many other surface science techniques.

The temperature rise as a function of depth in dental enamel irradiated at 9.6  $\mu\text{m}$  with 2- $\mu\text{sec}$  and 100- $\mu\text{sec}$  pulses was modeled (Fig. 6) using methods described in Materials and Methods, under Numerical Modeling. These simulations produced temperatures that reached nearly 2,500°C at the outer surface. Melting of dental enamel occurs between 800–1200°C, and vaporization occurs at greater temperatures; therefore, the model does not produce true temperatures above the melting point. It is expected that at tempera-

tures exceeding the melting point of enamel, some fraction of material will be ejected from the surface, resulting in a loss of deposited energy from the sample with a concomitant reduction in the thickness of the modified zone. Moreover, the rapid vaporization of mineral and spallation of molten mineral due to laser-generated stress transients are likely to result in the formation of the observed wavelike surface structures produced after several laser pulses are incident on the same spot (Fig. 7).

Despite these complications, the numerical calculations proved useful in predicting subsurface temperatures and the thickness of modification of dental enamel. Carbonate loss was negligible after a depth of 6  $\mu\text{m}$  for the 2- $\mu\text{sec}$  pulse and 11  $\mu\text{m}$  for the 100- $\mu\text{sec}$  pulse (Fig. 4). For each irradiating condition, the numerical simulation estimated the temperature at which carbonate is no longer lost to be 400–450°C. This is consistent with previous experiments performed using conventional heating [17]. Complete carbonate loss was not obtained until temperatures greater than 800°C were reached, which coincides with the minimum melting point of carbonated hydroxyapatite [33].

The laser energy is deposited in a layer whose thickness is defined by  $1/\mu_\alpha \approx 1.3 \mu\text{m}$  for  $\lambda = 9.6 \mu\text{m}$  light (Table 1). The thermal relaxation time,  $t = x^2/4K$ , corresponding to this absorption depth is approximately 1  $\mu\text{sec}$ . Since the pulse durations used in this study are longer than the thermal relaxation time, heat flows into the tooth during the pulse and a region is heated which is thicker than the absorption region. For the 2- $\mu\text{sec}$  pulse, the depth of treatment, approximately 2  $\mu\text{m}$ , is only slightly larger than the absorption depth. For the longer, 100- $\mu\text{sec}$  pulse, the depth of treatment is approximately 11  $\mu\text{m}$ .

The maximum temperature rise as a function of depth (Fig. 8) and the surface temperature rise as a function of time (Fig. 9) are depicted for dental enamel irradiated with a 2- $\mu\text{sec}$  pulse at 9.6 and 10.6  $\mu\text{m}$ . Since the 2- $\mu\text{sec}$  pulse duration is on the order of or less than the thermal relaxation time for each wavelength (Table 1), the predominant factor determining the thickness of the treated layer is the absorption coefficient.

At 9.6  $\mu\text{m}$ , the absorption depth is approximately 1.3  $\mu\text{m}$ , and at 10.6  $\mu\text{m}$  the absorption depth is approximately 12  $\mu\text{m}$  (Table 1). The maximum temperature rise in dental enamel irradiated at 9.6  $\mu\text{m}$  is much higher than that of enamel irradiated at 10.6  $\mu\text{m}$ , but the tempera-

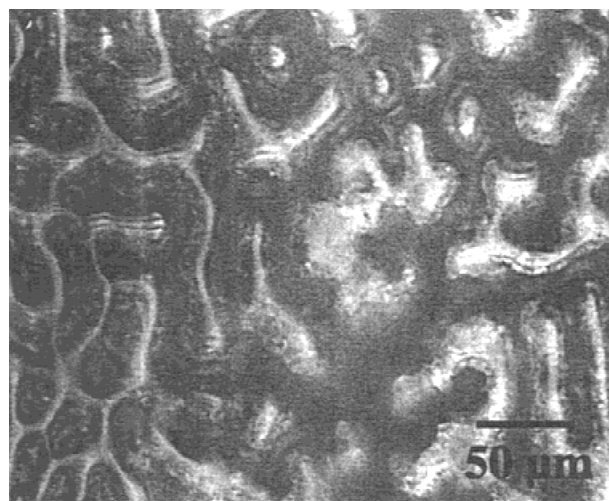


Fig. 7. Optical microscopy of the surface of dental enamel irradiated 50 times with a 2- $\mu\text{sec}$  pulse at 9.6  $\mu\text{m}$  with 2 J/cm<sup>2</sup>. The wavelike structures were likely formed from rapid vaporization of the mineral and spallation of molten enamel due to laser-generated stress transients.

ture rise also decays much more rapidly as a function of depth into the enamel. At 20- $\mu\text{m}$  depth, the calculated temperature of dental enamel irradiated with 10.6  $\mu\text{m}$  light is still almost 400°C; thus, some carbonate loss is expected deep into the tissue.

Greater carbonate loss at the surface was expected for dental enamel irradiated with 9.6  $\mu\text{m}$  light than for dental enamel irradiated with 10.6  $\mu\text{m}$  light due to the greater maximum temperature rise (Fig. 8). Experimentally, with either one pulse or five pulses, the carbonate loss was greater at all depths for the enamel irradiated at 10.6  $\mu\text{m}$  (Fig. 5). Total carbonate loss at the surface was achieved in five pulses at 10.6  $\mu\text{m}$ , but it took between 10–20 pulses for enamel irradiated at 9.6  $\mu\text{m}$ . Since the duration for which the surface temperature is above the melting point is much greater for enamel irradiated at 10.6  $\mu\text{m}$  than at 9.6  $\mu\text{m}$ , carbonate loss is also greater (Fig. 9).

From previous experience [13,34], carbonate loss was expected to depend upon the number of irradiating pulses, but the degree to which the dependence was exhibited experimentally was not expected. After irradiation, melting was present at the enamel surface for every set of conditions used in this study, e.g., 2 J/cm<sup>2</sup> with a 2- $\mu\text{sec}$  pulse at 9.6  $\mu\text{m}$  with one and 10 pulses (Fig. 10). The carbonate removal from the melted zone was expected to be very rapid, occurring on the same time scale as melting. Our original hypothesis

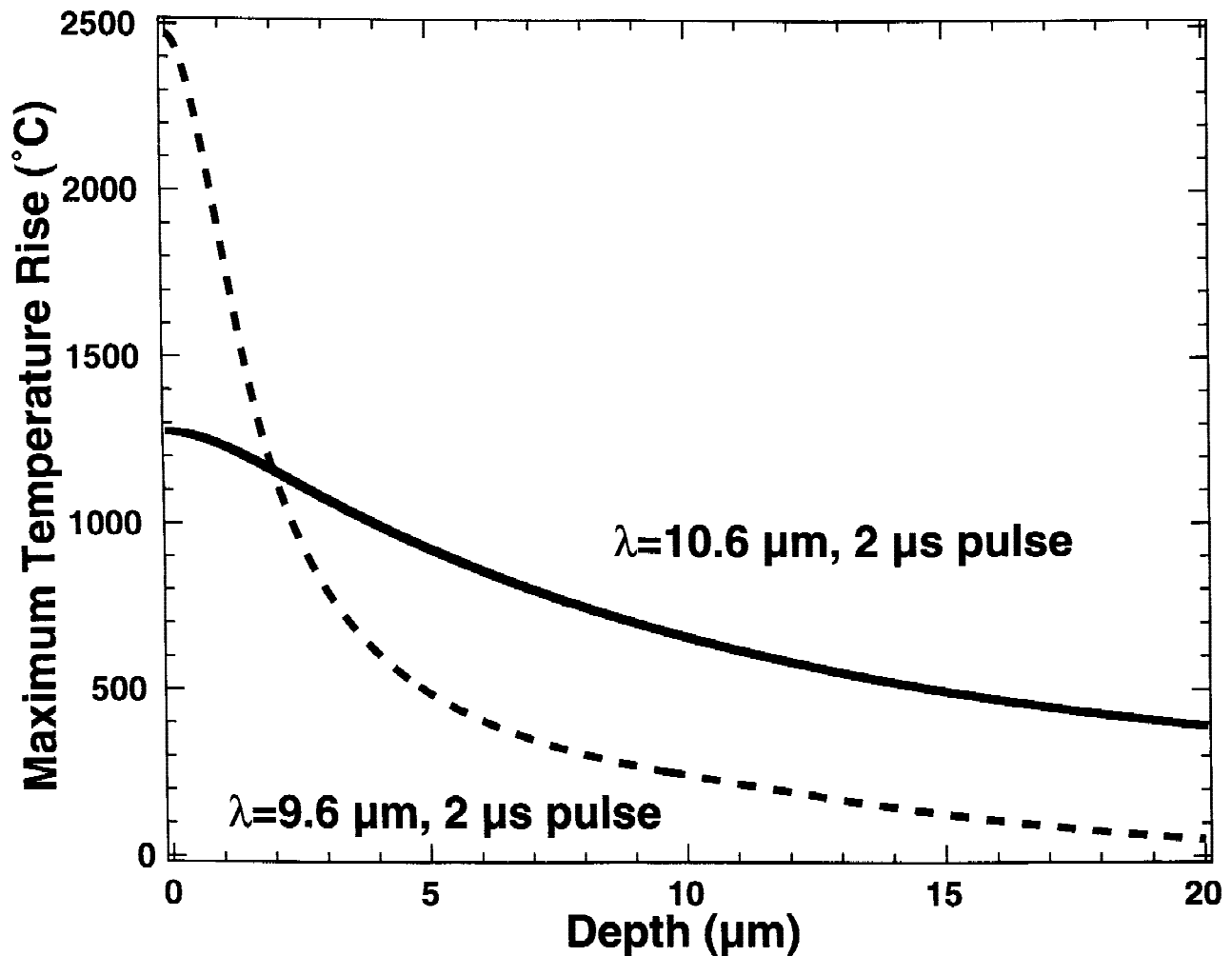


Fig. 8. The maximum temperature rise vs. depth was calculated for enamel irradiated with a 2-μsec pulse at 10.6 μm with 4 J/cm<sup>2</sup> (solid line) and at 9.6 μm with 2 J/cm<sup>2</sup> (dashed line).

was that at a given depth, the carbonate loss from laser-irradiated dental enamel could be estimated from the modeled maximum temperature rise in dental enamel. However, this hypothesis proved to be overly simplistic, since repeated temperature excursions above this threshold were required for complete elimination of carbonate from the enamel. From the maximum temperature rise determined in our numerical simulations, the percent carbonate loss as a function of depth can be estimated. Carbonate loss is initiated at 400°C, but complete carbonate loss does not occur until melting is achieved at temperatures greater than 800°C. To ensure carbonate loss, the enamel must be irradiated with a sufficient number of pulses, which depends upon the fluence and pulse duration of the laser irradiation and the absorption coefficient of dental enamel at the irradiation

wavelength. At this time, there are insufficient data to determine whether the duration of time at a certain temperature is the sole determining factor or if the kinetics of thermal cycling due to each individual pulse is also a contributing factor.

It is possible to precisely control the treatment depth of dental enamel in two different ways. In the first method, the pulse duration can be varied. A shorter pulse will treat a thinner layer near the surface, but the minimum treatment depth is limited by the absorption depth of the laser light. In the second method, the wavelength of laser irradiation can be changed, which affects the absorption depth of the material. Different depths can be treated in this manner, but the pulse duration limits the minimum depth treated by this method. By using a highly absorbed laser wavelength such as 9.6 μm, the

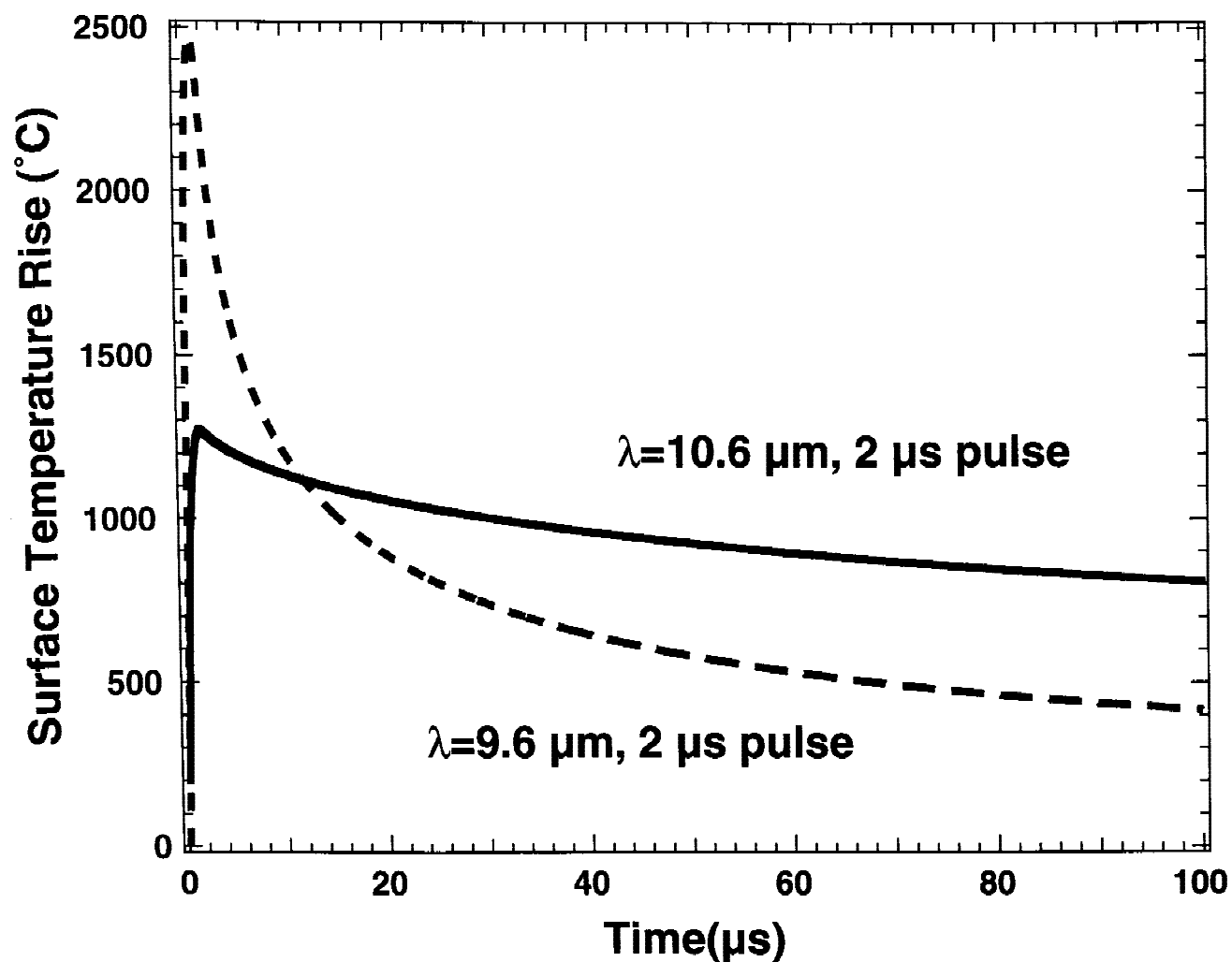
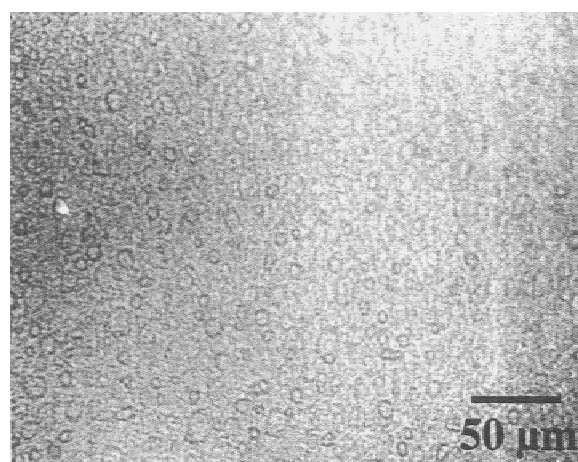
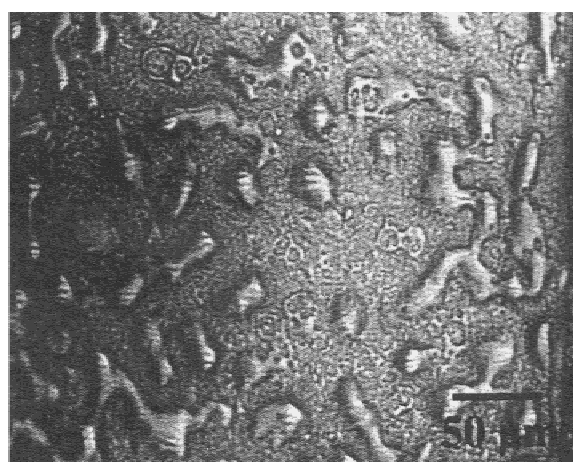


Fig. 9. The surface temperature rise vs. time was calculated for enamel irradiated with a 2- $\mu\text{sec}$  pulse at  $10.6 \mu\text{m}$  with  $4 \text{ J/cm}^2$  (solid line) and at  $9.6 \mu\text{m}$  with  $2 \text{ J/cm}^2$  (dashed line).



(a)



(b)

Fig. 10. Optical microscopy of the surface of dental enamel irradiated at  $9.6 \mu\text{m}$  with a 2- $\mu\text{sec}$  pulse and fluence of  $2 \text{ J/cm}^2$  was melted after a single pulse (a). The surface was modified to a much greater extent after 10 pulses (b).

depth of treatment can be changed from a minimum of 2  $\mu\text{m}$  with a 2- $\mu\text{sec}$  or shorter pulse up to any depth needed, provided the proper pulse duration is obtainable.

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